HYDROGEN-ABSORBING ALLOY, METHOD OF SURFACE MODIFICATION OF THE ALLOY, NEGATIVE ELECTRODE FOR BATTERY AND ALKALINE SECONDARY BATTERY

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a division of U.S. patent application Ser. No. 08/787,101, filed Jan. 22, 1997 now U.S. Pat. No. 5,962,165 which is a continuation-in-part of U.S. patent application Ser. No. 08/505,154, filed Jul. 21, 1995, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to a hydrogen-absorbing alloy, a method of modifying the surface of the hydrogen-absorbing alloy, negative electrode for battery and an alkaline secondary battery.

Hydrogen-absorbing alloy is known as being capable of stably absorbing and storing hydrogen several ten thousands times (calculated as a gas under normal temperature and pressure) as much as of its own volume. Therefore, hydrogen-absorbing alloy is noticed as a promising material for safely and easily storing, keeping and transporting hydrogen as an energy source. Hydrogen-absorbing alloy is also studied for utilization in a chemical heat pump or compressor by making most of a difference in property between hydrogen-absorbing alloys, some of them being developed for actual use. Recently, the application of hydrogen-absorbing alloys to a metal hydride secondary battery (for example, nickel-hydrogen secondary battery) as an energy source by making use of hydrogen stored in a hydrogen-absorbing alloy, as well as an electrode material by making use of its high catalytic activity in the absorption and desorption reaction of the hydrogen-absorbing alloys has been extensively developed.

As evident from these facts, the hydrogen-absorbing alloy has many possibilities for various applications in view of its physical and chemical characteristics, so that the hydrogen-absorbing alloy is now considered as being one of important raw materials in future industrial.

The metal capable of absorbing hydrogen and constituting the hydrogen-absorbing alloy may be in the form of single substance which reacts exothermically with hydrogen, i.e., a metal element capable of forming a stable compound together with hydrogen (for example, platinum group elements, lanthanum group elements and alkaline earth elements); or in the form of an alloy comprising such a metal, as mentioned above, alloyed with another kind of metals. One of the advantages of the alloy resides in that the bonding strength between a metal and hydrogen can be suitably weakened so that not only the absorption reaction but also the desorption reaction can be performed comparatively easily. Second advantage of the alloy resides in that the absorption and desorption characteristics of the alloy with respect to the magnitude of hydrogen gas pressure required for the reaction (equilibrium pressure; plateau pressure), the extent of equilibrium region (plateau region), the change (flatness) of equilibrium pressure during the process of absorbing hydrogen and the like can be improved. Third advantage of the alloy resides in the improvement in chemical and physical stability.

The composition of the conventional hydrogen-absorbing alloy may be classified into the following types; i.e., (1) an AB_5 type (for example, $LaNi_5$, $CaNi_5$); (2) an AB_2 type (for example, $MgZn_2$, $ZrNi_2$); (3) an AB type (for example, TiNi, TiFe); (4) an A_2B type (for example, Mg_2Ni, Ca_2Fe); and other types (for example, cluster), wherein A represents a metal element which is capable of exothermically reacting with hydrogen, and B, another kind of metal. Among them, $LaNi_5$ of (1), a laves phase alloy belonging to (2) and some kinds of alloy belonging to (3) are capable of reacting with hydrogen at the normal temperature, and chemically stable so that they are extensively studied as a candidate for an electrode material of a secondary battery.

Whereas, the hydrogen-absorbing alloy belonging to (4) A_2B type is accompanied with the following problems. Namely, the alloy strongly attract hydrogen so that hydrogen once absorbed therein can be hardly released. The absorption and desorption reaction thereof occurs only when the temperature thereof is raised up to a relatively high degree (about 200 to 300° C.), and the rate of the reaction, if occurred, is slow. The chemical stability, in particular the stability in an aqueous solution, of the alloy is comparatively low. The alloy is generally very viscous and hard so that the working such as pulverization of it is very difficult. In view of these facts, the hydrogen-absorbing alloy of A_2B type is rarely utilized except for the storage and transport of hydrogen in spite of its excellent capacity of absorbing hydrogen which is comparable to other types of hydrogen-absorbing alloy on the basis of volume and, if calculated on the basis of weight, two to several times as high as that of other types of hydrogen-absorbing alloy. Therefore, of these problems inherent to the hydrogen-absorbing alloy of A_2B type as explained above are solved, it would be possible to expand the application of the alloy not only to the same fields as those of other types of hydrogen-absorbing alloy but also to a new field of utilization.

By the way, there have been reported a number of academic papers on the hydrogen-absorbing alloy of this (5) type. However, up to date, the report of practical use or testing for practical use is almost none.

Meanwhile, there is disclosed in Jpn. Pat. KOKAI Publication No. 6-76817 a magnesium-based hydrogen-absorbing alloy represented by a composition formula of $Mg_{2-x}Ni_{1-y}A_yB_z$ (wherein x is 0.1 to 1.5; y is 0.1 to 0.5; A represents an element selected from Sn, Sb and Bi; B represents an element selected from Li, Na, K and Al) such for example as $Mg_{1.5}Al_{0.5}Ni_{0.7}Sn_{0.3}$; or $Mg_{1.8}Al_{0.2}Ni_{0.8}Sn_{0.2}$. There is also disclosed in this publication that the hydrogen-absorbing alloy can be utilized as a negative electrode material of an alkali secondary battery. However, since this hydrogen-absorbing alloy disclosed in the publication is fundamentally of A_2B type, the hydrogen-absorbing and desorbing property thereof in the normal temperature region is poor. Therefore, in order to make it possible to absorb and desorb hydrogen under normal temperature and pressure, the hydrogen-absorbing alloy is covered on the surface thereof with a nickel metal compound or a phosphorous compound as disclosed in the publication.

As explained above, the A_2B type hydrogen-absorbing alloy has a feature distinct from other types of hydrogen-absorbing alloy in that it is light in weight, large in capacity and low in raw material cost since its composition is mainly consisted of alkaline earth metals and iron group elements. However, the A_2B type hydrogen-absorbing alloy is accompanied with various problems as explained above.

BRIEF SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a hydrogen-absorbing alloy which is chemically